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# Bifunctional Imidazolium-Based Ionic Liquid Decorated UiO-67 Type MOF for Selective $CO_2$ Adsorption and Catalytic Property for $CO_2$ Cycloaddition with Epoxides

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**S** Supporting Information

**ABSTRACT:** A bifunctional robust and highly porous imidazolium-based ionic liquid decorated UiO-67 type MOF (UiO-67-IL, 1) was successfully constructed via solvothermal assembly of the imidazolium-based ligand and Zr(IV) ions. It exhibits a highly selective adsorption for CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub>. Furthermore, 1 herein can be used as a highly active heterogeneous catalyst for CO<sub>2</sub> cycloaddition with epoxides under atmospheric pressure with or without cocatalyst TBAB (*n*-Bu<sub>4</sub>NBr).



## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>), accumulating in the atmosphere at an alarming rate, is deemed as the major greenhouse gas causing global warming over the past several decades.<sup>1</sup> In order to reduce the greenhouse effect, CO<sub>2</sub> capture and storage/ sequestration (CCS) and its chemical transformation are areas of intense current interest.<sup>2</sup> For overcoming these two great challenges, synthetic porous materials are currently used to adsorb and store CO<sub>2</sub>.<sup>3</sup> On the other hand, catalytic CO<sub>2</sub> conversion into value-added industrial products can make waste CO<sub>2</sub> be an abundant, nontoxic, and inexpensive C1 building block.<sup>2a</sup> Although recent progress on both CCS and catalytic CO<sub>2</sub> conversion is remarkable,<sup>4</sup> bifunctional materials which are able to incorporate both selective CO<sub>2</sub> adsorption and catalytic conversion are still rarely reported.

It is known that metal–organic frameworks (MOFs) have high porosity, tunable composition and pore surface, so they might be promising porous materials for selective gas adsorption and effective heterogeneous catalysts.<sup>5</sup> Recently, a postsynthetic method was proposed and widely used as a powerful tool to modify and enhance the functionality of MOFs.<sup>6</sup> However, the postsynthetic yields, especially for the organic functional group transformation, are usually not that ideal, which results from the inherent imperfection of the heterogeneous solid–liquid reactions. Thus, the synthesis of the desired MOFs based on the premodified ligands could be an alternative approach to solve this problem. Recently, room-temperature ionic liquids (ILs) have attracted much attention owing to their unique properties such as nonvolatility, nonflammability, and recyclability.<sup>7</sup> Specifically, some ILs, for example, imidazolium-based polymeric ionic liquids, have been demonstrated to be a unique species in the CO<sub>2</sub> chemical fixation and useful catalysts for the cycloaddition of CO<sub>2</sub> to epoxides.<sup>8</sup> In principle, ILs such as imidazolium-based IL units can be grafted and immobilized in MOFs via ligand functionalization. In this way, the advantages of MOFs and ILs would be combined together to lead to the expected multifunctional porous materials for CO<sub>2</sub> selective adsorption and its chemical transformation under mild conditions.

We recently reported a series of functional NMOFs via postsynthetic approach.<sup>9</sup> Therein, imidazolium-containing MOFs are demonstrated to be a highly active class of triphase catalysts for the azidation and thiolation between aqueous/ organic phases.<sup>9b</sup> The imidazolium decoration yields that were achieved via postsynthesis functionalization of a Cd(II)-MOF, however, are only within a range of 60–70%. Different from our previous case, we report herein a new imidazolium-based UiO-67 type MOF (UiO-67-IL, 1) via direct ligand functionalization (Scheme 1). Compared to a postsynthetic approach, the IL-functionalized yield based on this ligand modification method is quantitative and the resulting MOF

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#### Scheme 1. Synthesis of UiO-67-IL (1)



material thereby presents high-density IL active sites. In addition,  $CO_2$  adsorption and separation selectivity over  $N_2$  and  $CH_4$  was preliminarily explored on **1**. More interestingly, UiO-67-IL (**1**) exhibits an excellent catalytic performance for efficient chemical transformation of  $CO_2$  to cyclic carbonates under atmospheric pressure (1 atm).

#### EXPERIMENTAL SECTION

Materials and Instrumentations. All the chemicals were obtained from commercial sources (Acros) and used without further purification. <sup>1</sup>H NMR data were collected on a Bruker Avance-400 spectrometer. Chemical shifts are reported in  $\delta$  relative to TMS. Infrared spectra were obtained in the 400-4000 cm<sup>-1</sup> range using a Bruker ALPHA FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer model 2400 analyzer. ICP measurement was performed on an IRIS Interpid (II) XSP and NU AttoM. HRMS analysis was carried out on a Bruker maXis UHR-TOF ultrahigh resolution quadrupole-time-of-flight mass spectrometer. Thermogravimetric analyses were carried out on a TA Instruments Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10 °C/min. The XRD pattern was obtained on D8 ADVANCE X-ray powder diffractometer (XRPD) with Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDS).

Synthesis of Intermediate A. 4-Bromo-3-methylbenzoic acid (5.00 g, 23.40 mmol), 4-carboxyphenylboronic acid (4.80 g, 28.90 mmol), K<sub>2</sub>CO<sub>3</sub> (25.80 g), and tetrakis(triphenylphosphine)palladium (1.50 g) were added to a toluene/ethanol/water solution (50 mL, 1:1:1, v/v). The reaction was conducted with reflux for 24 h with magnetic stirring. The pH value of aqueous phase was adjusted to 2.0 by diluted hydrochloric acid (1M), followed by the esterification with methanol (75 mL) at reflux for 12 h in the presence of concentrated sulfuric acid (5 mL). After that, the pH of the reactant solution was adjusted to 7.0 by saturated solution of sodium carbonate. The product was collected and dried in vacuum to generate A (5.35 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.30 (3H, s, -CH<sub>3</sub>), 3.95 (6H, s, -OCH<sub>3</sub>), 7.26-8.12 (7H, m, -Ar). FTIR (KBr, cm<sup>-1</sup>): 3100 (w), 2950 (s), 2844 (m), 1712 (s), 1602 (s), 1552 (m), 1461 (m), 1108 (m), 762 (m). ESI-MS: calcd for  $C_{17}H_{16}O_4$  M<sup>+</sup>, m/z284.10, found, m/z 284.11.

**Synthesis of B.** A mixture of intermediate A (2.54 g, 8.96 mmol), N-bromosuccinimide (1.83 g, 10.30 mmol), AIBN (0.15 g, 0.90 mmol), and benzene (45 mL) was stirred at 80 °C for 12 h. After removal of the solvent in vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether-dichloromethane (1:1 v/v) as the eluent to generate B (1.45 g, 45%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 3.91 (6H, s,  $-OCH_3$ ), 4.69 (2H, s,  $-ArCH_2Br$ ), 7.45–8.30 (7H, m, -Ar). FTIR (KBr, cm<sup>-1</sup>): 3100 (w), 2956, 2838 (m), 1720 (s), 1602 (m), 1552 (m), 1461 (m), 1116 (m), 763 (m), 627 (m). ESI-MS: calcd for C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>Br M<sup>+</sup>, *m*/*z* 362.02; found, *m*/*z* 362.17.

**Synthesis of C.** A mixture of intermediate **B** (1.45 g, 4.00 mmol), 1-allylimidazole (0.95 g, 8.80 mmol), and acetonitrile (45 mL) was stirred at 80 °C for 2 h. After removal of the solvent in vacuum, the residue was purified by column chromatography on silica gel using dichloromethane–methanol (20:1, v/v) as the eluent to generate **C** as yellow oil (1.33 g, 85%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$  (ppm):

3.90 (6H, s,  $-OCH_3$ ), 4.74 (2H, q,  $-NCH_2CH$ ), 5.19, 5.33 (2H, d,  $-CHCH_2$ ), 5.54 (2H, s,  $-NCH_2Ar$ ), 5.89 (1H, m,  $-CH_2CHCH_2$ ), 7.63, 8.01 (2H, d, -NCHCHN-), 7.42–7.52, 8.03–8.11 (7H, m, -Ar), 8.80 (1H, s, -NCHN). FTIR (KBr, cm<sup>-1</sup>): 3167 (m), 3054 (m) 2956 (m), 2896 (m), 2836 (m), 1712 (s), 1529 (w), 1604 (w), 1556 (w), 1123 (m), 905 (m), 762 (m). ESI-MS: calcd for  $(C_{23}H_{23}N_2O_4)^+$  M<sup>+</sup>, m/z 391.17; found, m/z 391.16.

**Synthesis of L.** C was hydrolyzed by LiOH (10 equiv) in a methanol/water (3:1, v/v) at room temperature (12 h). Then the pH value of the reaction solution was adjusted to 2–3 by hydrobromic acid. The product precipitated from the solution to generate imidazolium-based ligand L as white crystalline solids in 90% yield. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$  (ppm): 4.74 (2H, q,  $-NCH_2CH$ ), 5.19, 5.33 (2H, d,  $-CHCH_2$ ), 5.53 (2H, s,  $-NCH_2Ar$ ), 5.89 (1H, m,  $-CH_2CHCH_2$ ), 7.63, 8.00 (2H, d, -NCHCHN-), 7,42–7.49, 8.02–8.08 (7H, m, -Ar), 8.82 (s, -NCHN), 13.12 (2H, s, -COOH). FTIR (KBr, cm<sup>-1</sup>): 3377 (s), 3160, 3092 (m), 2859 (m), 2776 (m), 1717 (s), 1529 (w), 1604 (m), 1556 (m), 1100 (m), 987 (m), 920 (m), 769 (m). ESI-MS: calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>Br, M<sup>+</sup>, *m/z* 442.05; found, *m/z* 442.04.

Synthesis and Characterization of UiO-67-IL (1). ZrCl<sub>4</sub> (28.80 mg, 0.12 mmol) and 50 equiv of acetic acid (0.34 mL) were dissolved in DMF (5 mL) by using ultrasound for about 10 min. The linker (43.56 mg, 0.12 mmol) was added to the clear solution in an equimolar ratio with regard to ZrCl<sub>4</sub>. The tightly capped flasks were kept in an oven at 120 °C under static conditions. After 24 h, the reaction system was cooled to room temperature and the precipitate was isolated by centrifugation. The solids were suspended in fresh DMF (10 mL). After standing at room temperature for 5 h, the suspension was centrifuged and the solvent was decanted off. The obtained particles were washed with ethanol (10 mL) several times in the same way as described for washing with DMF. Finally, the solids were dried under reduced pressure to generate the as synthesized UiO-67-IL (1) crystals. Yield, 69.2%. IR (KBr, cm<sup>-1</sup>): 3077 (m), 1604 (m), 1552 (m), 1522 (w), 1424 (s), 1146 (m), 780 (m), 657 (m). Elemental analysis (%) calcd for C<sub>21</sub>H<sub>196</sub>Zr<sub>1</sub>N<sub>2</sub>O<sub>53</sub>Br<sub>1</sub> (desolvated): C 45.32, H 3.54, N 5.04, Zr 16.37, Br 14.39. Found: C 43.87, H 3.58, N 4.98, Zr 16.86, Br 14.24.

**Adsorption Measurements.** Gas adsorption experiments were carried out with a Micromeritics ASAP 2020/TriStar 3000 volumetric gas sorption instrument. Prior to the measurement, the sample was soaked in ethanol for 48 h to exchange DMF solvent molecules; after centrifugation and drying, the sample was loaded in a sample tube and dried under high vacuum at 393 K for 10 h to remove the residual solvent molecules in the channel. About 200 mg of the dissolved sample was used for the entire adsorption measurement. The nitrogen sorption isotherm was collected at 77 K in a liquid nitrogen bath, in order to study its permanent porosity and robustness. For selective adsorption evaluation, the gas sorption experiments of  $CO_2$ ,  $N_2$ , and  $CH_4$  were carried out at 273 K in an ice—water bath, and at 298 K in a temperature controlled circular bath, respectively.

**Isosteric Heat Adsorption.** The isosteric heat of adsorption represents the strength of the interactions between adsorbate molecules and the adsorbent lattice atoms and can be used as a measurement of the energetic heterogeneity of a solid surface. The isosteric heat of adsorption at a given amount can be calculated by the Clausius–Clapeyron equation as

$$Q_{\rm st} = -RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_{n_{\rm a}}$$

where  $Q_{st}$  is the isosteric heat of adsorption (kJ/mol), *P* is the pressure (kPa), *T* is the temperature, *R* is the gas constant, and  $n_a$  is the adsorption amount (mmol/g).

**Calculations of the Adsorption Selectivity.** The selectivity of the preferential adsorption of component 1 over component 2 in a binary mixture containing 1 and 2 can be formally defined as

$$S_{\rm ads} = \frac{q_1 / q_2}{P_1 / P_2}$$



"(i) 4-Carboxyphenylboronic acid,  $K_2(CO_3)_2$ , tetrakis(triphenylphosphine)palladium, toluene/ethanol/water solution (1:1:1, v/v), reflux, 24 h. (ii) MeOH/H<sub>2</sub>SO<sub>4</sub>, reflux, 12 h. (iii) N-Bromosuccinimide, AIBN, benzene, 80 °C, 12 h. (iv) 1-Allylimidazole, CH<sub>3</sub>CN, 80 °C, 2 h. (v) LiOH/MeOH-H<sub>2</sub>O (rt, 12 h), HBr.



Figure 1. (a) Simulated PXRD pattern of UiO-67 and measured PRXD pattern of UiO-67-IL (1). (b) SEM image of 1. (c) Dynamic light scattering (DLS) measurement of 1. (d) TGA trace of UiO-67-IL (1) and its PRXD pattern after heating at 200  $^{\circ}$ C for 1 h.



Figure 2. Left: Nitrogen sorption isotherms of 1 and UiO-67. Right: Density functional theory pore-size distribution for UiO-67 and 1 determined from their nitrogen adsorption isotherms at 77 K.

where  $q_1$  and  $q_2$  are the absolute loadings. In all of the calculations to be presented below, the calculations of  $S_{ads}$  are based on the use of the ideal adsorbed solution theory (IAST) of Myers and Prausnitz. These calculations are carried out using the pure-component isotherm fits of absolute loadings.

**Catalytic Cycloaddition of CO<sub>2</sub> with Epoxides.** The solventfree cycloaddition reaction was carried out in a flask (10 mL) with magnetic stirrer with known amounts of epoxides, catalyst (UiO-67-IL, 1), and cocatalyst (TBAB) charged into the reactor. The reactor was conducted at a desired temperature, and CO<sub>2</sub> was added through a balloon under 1 atm of pressure. With epichlorohydrin and styrene oxide as model substrate, the effect of temperature, reaction times, and amount of catalyst and cocatalyst on the performance were systematically investigated for the utilization of  $CO_2$  for useful high-value chemicals.

**Catalyst Regeneration.** After each catalytic cycle, **1** was recovered by centrifugation, then rinsed with ethanol, and dried in vacuum at 90 °C for the next catalytic run under the same reaction conditions.

**Leaching Test.** The solid catalyst 1 was separated from the hot reaction solution right after reaction for 2.5 h. The reaction was continued with the filtrate in the absence of 1 for an additional 9.5 h. No further increase in the yield of cyclic carbonate was detected, which confirms the catalytically active sites for this  $CO_2$  cycloaddition of epichlorohydrin located on 1.



Figure 3. Left: CO2, CH4, and N2 adsorption isotherms of 1 at 273 K. Right: CO2, CH4, and N2 adsorption isotherms of UiO-67-IL at 298 K.



**Figure 4.** Left: Isosteric heat of adsorption for  $CO_2$  at different  $CO_2$  loadings. Middle: Pressure-dependent selectivity profiles on 1 calculated by the IAST method for  $CO_2/N_2$  (50:50) and  $CO_2/CH_4$  (50:50) binary mixtures at 273 K. Right: Pressure-dependent selectivity profiles on 1 calculated by the IAST method for  $CO_2/N_2$  (50:50) and  $CO_2/CH_4$  (50:50) binary mixtures at 298 K.

#### RESULTS AND DISCUSSION

**Ligand Synthesis.** As shown in Scheme 2, ligand L with imidazolium unit was synthesized as white crystalline solids. The ligand backbone of A was obtained by the palladium-catalyzed C–C coupling reaction between 4-bromo-3-methylbenzoic acid and 4-carboxyphenylboronic acid. After ester-

Table 1. 1-Catalyzed  $CO_2$  Cycloaddition with Epichlorohydrin with or without TBAB  $(n-Bu_4NBr)^a$ 

	CI	+ CO <sub>2</sub> (1 atr	n) 1 or 1/			
entry	1(% mol) <sup>b</sup>	TBAB (% mol)	$T(^{\circ}C)$	<i>t</i> (h)	yield (%) <sup>c</sup>	TOF
1	0.7		25	48	3	0.09
2		1.0	25	48	21	
3	0.7	1.0	25	48	80	2.28
4	0.7	1.0	25	72	93	1.76
5	0.7	1.0	50	3	77	35.06
6	0.7	1.0	90	3	99	45.08
7	0.7		50	3	28	12.75
8	0.7		50	8	53	9.05
9	0.7		50	12	68	7.74
10	0.7		50	48	80	2.28
11	0.7		90	3	75	34.15
12	0.7		90	8	88	13.66
13	0.7		90	12	88	10.02
14	1.5		90	3	81	18.00
15	1.5		90	8	95	7.92
16	1.5		90	12	95	5.28

"Reaction conditions: epichlorohydrin, 1 atm of CO<sub>2</sub>. <sup>b</sup>Calculated based on the number of active sites in 1. <sup>c</sup>The yields were determined by <sup>1</sup>H NMR spectra.

ification, the bromination reaction was carried out with NBS in benzene to generate **B**. The imidazolium group was introduced by the reaction of substituted benzyl bromide **B** with 1allylimidiazole to provide **C**. Dicarboxylic ligand **L** was obtained via hydrolyzation of **C** by LiOH in MeOH/H<sub>2</sub>O mixed solvent system at room temperature in good yield. The corresponding <sup>1</sup>H NMR, FTIR, and MS spectra for **A**, **B**, **C**, and **L** are provided in the Supporting Information.

Synthesis and Characterization of UiO-67-IL (1). UiO-67-IL (1) was prepared according to the reported method.<sup>10</sup> As indicated in Scheme 1, ZrCl<sub>4</sub> and L reacted in DMF under solvothermal conditions (120 °C, 24 h) to yield a buffy crystalline powder of UiO-67-IL (1). The powder X-ray diffraction (PXRD) pattern indicates that 1 is highly crystalline and its structure is identical to that of pristine UiO-67 (Figure 1).<sup>10c</sup> So the introduced imidazolium group did not affect the UiO-67 framework formation under the reaction conditions. Scanning electronic microscopy (SEM) measurement shows that 1 was obtained as uniform nanoscale particles (ca. 363 nm), and they showed a regular octahedral shape (Figure 1), which is further supported by the dynamic light scattering (DLS) measurement (Figure 1). In addition, thermostability of 1 was examined by thermogravimetric analysis (TGA) and PXRD measurement. The evacuated sample of 1 was heated at ca. 200 °C for 1 h; no framework collapse was observed (Figure 1), although this decomposition temperature is significantly lower than that of its pristine UiO-67 (decomposition at 520 °C).<sup>10d</sup> The thermostability of 1 is good enough to be the heterogeneous catalyst for most organic transformations.

To examine the permanent porosity,  $N_2$  adsorption property of 1 was measured at 77 K (Figure 2). It is similar to that of UiO-67; 1 also exhibits type I isotherms, featuring characteristics of microporous materials. The  $N_2$  absorption amount of 1 was 284 cm<sup>3</sup>/g, and its Brunauer–Emmett–Teller (BET)

Entry	Epoxide	Cyclic carbonate	MOFs [% mol]	TBAB [% mol]	Yield $[\%]^b$	
1	<u>^</u>		1.5		95	
2		CI	0.7	1	99	
3	<u>^</u>	o construction of the second s	1.5		97	
4	Br	Br	0.7	1	99	
5			1.5		51	
6		$\bigcirc$	0.7	1	98	
7			1.5		52	
8		$\mathcal{O}^{*}$	0.7	1	99	
9			1.5		6	
10		$\swarrow$ $\int_{3}$	$\bigvee$	0.7	1	72

Table 2. Yields of Various Cyclic Carbonates Prepared from the Cycloaddition of  $CO_2$  with Corresponding Epoxides Catalyzed by 1 with and without TBAB<sup>*a*</sup>

<sup>*a*</sup>Reaction conditions: for catalyst 1, 12 h, 90 °C, CO<sub>2</sub> 1 atm. For catalyst 1–TBAB, 3 h, 90 °C, CO<sub>2</sub> 1 atm. <sup>*b*</sup>The yields were determined by <sup>1</sup>H NMR spectra (Supporting Information).

Tal	ble 3.	UiO-67	or	UiO	)-67-	TBAB	Catal	yzed
Epi	ichlor	ohydrin	CO	$_{2}$ C	ycloa	additio	n <sup>a</sup>	

entry	catalyst	catalyst (mol %)	cocatalyst (mol %)	<i>t</i> (h)	conversion (%)	TOF	
1	UiO- 67	1.5	none	3	<3		
2	UiO- 67	1.5	none	8	<3		
3	UiO- 67	1.5	none	14	8	6.67	
4	UiO- 67	0.7	TBAB, 1	3	46	22.03	
5	UiO- 67	0.7	TBAB, 1	8	82	18.22	
6	UiO- 67	0.7	TBAB, 1	14	98	8.09	
<sup><i>a</i></sup> Reaction conditions: solvent free, CO <sub>2</sub> (1 atm), 90 °C.							

surface area was found to be 846 m<sup>2</sup>/g. These values are significantly smaller than those of pristine UiO-67 (N<sub>2</sub> absorption amount, 710 cm<sup>3</sup>/g; surface area, 2113 m<sup>2</sup>/g). The corresponding pore volume of 1 based on the maximum nitrogen adsorption is 0.43 cm<sup>3</sup>/g (Figure 2), which is less than half compared with its parent UiO-67 (1.08 cm<sup>3</sup>/g). Such differences are clearly caused by the introduced imidozalium groups which inevitably occupy the framework pores' place.

**CO**<sub>2</sub> **Selective Adsorption.** Considering high porosity together with the incorporation of exposed Lewis acid sites and the high-density imidazolium groups within 1, its adsorption isotherms on the evacuated 1 for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> were examined, respectively. As illustrated in Figure 3, 1 gives a CO<sub>2</sub> uptake amount of 22.4 cm<sup>3</sup> g<sup>-1</sup> at 298 K and 47.7 cm<sup>3</sup> g<sup>-1</sup> at

273 K under 1 atm, which is similar to the reported  $CO_2$  loading amount for UiO-67 (22.9 cm<sup>3</sup> g<sup>-1</sup> at 298 K, and 48.6 cm<sup>3</sup> g<sup>-1</sup> at 273 K) under the same conditions.<sup>5c,10d</sup> Compared to UiO-67, no decrease in  $CO_2$  uptake capacity of 1 was observed although the involved large-sized imidazolium groups have led to largely decreased surface area and pore volume in 1 as mentioned above.

Differently from CO<sub>2</sub> uptake, only a small amount of CH<sub>4</sub>  $(6.0 \text{ cm}^3 \text{ g}^{-1})$  or N<sub>2</sub>  $(1.2 \text{ cm}^3 \text{ g}^{-1})$  uptake was observed based on 1 at 298 K under 1 atm pressure. As we know, isosteric analysis of CO<sub>2</sub> adsorption isotherms collected at various temperatures allows an estimation of the coverage-dependent isosteric heat of adsorption  $(Q_{st})$ ,<sup>10d</sup> where the behavior of this function is determined by the relative magnitudes of the adsorbent-adsorbate and adsorbate-adsorbate interactions. On the basis of CO<sub>2</sub> adsorption isotherms at 273 and 298 K, the Qst of CO2 was then calculated by the virial method (Supporting Information). As shown in Figure 4, the  $Q_{st}$  value for 1 is 25–27 kJ mol<sup>-1</sup>, being much higher than that of 15.8– 15.9 kJ mol<sup>-1</sup> for UiO-67.<sup>10d</sup> The higher  $Q_{st}$  of 1 can be ascribed to the high density of open imidazolium sites on 1. To predict the selective CO<sub>2</sub> separation performance over N<sub>2</sub> and  $CH_4$  at 298 K, the selectivity for 50:50  $CO_2/CH_4$  and  $CO_2/N_2$ binary mixtures was estimated up to 1 atm from the singlecomponent gas-adsorption isotherms utilizing ideal adsorbed solution theory (IAST) based on a dual-site Langmuir-Freundlich (DSLF) simulation. As indicated in Figure 4, the  $CO_2/CH_4$  selectivity of 1 calculated for a 50:50  $CO_2/CH_4$ mixture is 4.9 at 1 atm and 273 K, and the CO<sub>2</sub>/N<sub>2</sub> selectivity calculated for a 50:50 CO<sub>2</sub>/N<sub>2</sub> mixture is 33.3 at the same conditions. The selectivity for  $CO_2/CH_4$  and  $CO_2/N_{24}$ 



**Figure 5.** Left: Reaction time examination (black line) and leaching test (red line) for  $CO_2$  cycloaddition of epichlorohydrin catalyzed by 1. Reaction conditions: solvent free,  $CO_2$  (1 atm), 90 °C, 1 (1.5, mol %). The solid catalyst of 1 was filtrated from the reaction solution after 2.5 h, whereas the filtrate was transferred to a new vial and reaction was performed under the same conditions for an additional 9.5 h. Middle: Recycling catalytic test. Yields obtained at 8 h in repeated runs of the  $CO_2$  cycloaddition with epichlorohydrin catalyzed by 1 (solvent free,  $CO_2$  (1 atm), 90 °C, 1 (1.5, mol %)). Yield %: run 1, 99%; run 2, 99%; run 3, 97%; run 5, 96%. Right: Corresponding PXRD patterns for each catalytic cycle.

Table 4. Summary of the Reported CO<sub>2</sub> Cycloaddition of Epichlorohydrin Catalyzed by MOFs and MOF–TBAB Catalytic Systems

entry	catalyst	catalyst (mol %)	cocatalyst (mol %)	<i>t</i> (h)	P (MPa)	T (°C)	yield (%)	ref
1	USTC-253-TFA	1	TBAB, 6.5	72	0.1	25	38.2	12
2	ZIF-8	2.4	none	4	0.7	100	98.2	13
3	CHB(M)	1.6	TBAB, 1.6	6	1.2	80	89.2	14
4	MOF-5	0.3	TBAB, 2.5	12	0.1	50	93	15
5	$(Cu_4L_1)n$	0.2	TBAB, 10	48	0.1	25	85	16
6	HKUST-1	0.2	TBAB, 10	48	0.1	25	56	16
7	IL-ZIF-90	0.49	none	3	1	120	94	17
8	UMCM-1-NH <sub>2</sub>	0.64	TBAB, 0.64	24	1.2	25	55	18
9	Ni-MOF	1	TBAB, 3	4	2	100	84	19
10	MMPF-18	0.25	TBAB, 7	48	0.1	25	99	20
11	$Cu_3(BTC)_2$	2.74	TBAB, 10	4	0.7	100	63.8	21
12	Meim-UiO-66	0.745	none	24	0.1	120	93	22
13	UiO-67-IL (1)	0.7	TBAB, 1	3	0.1	90	99	this work
14	UiO-67-IL (1)	1.5	none	8	0.1	90	95	this work

however, is as high as 7.6 and 381.4 at 1 atm and 298 K, respectively (Figure 4). On the basis of measured adsorption data for 1 and UiO-67 collected at 273 and 298 K, there is a clear affinity for  $CO_2$  according to the order 1 > UiO-67, which clearly resulted from the introduced imidazolium functional groups.

 $\overline{CO_2}$  Cycloaddition Catalyzed by 1 and 1–TBAB. With the above information in hand, we set out to study the catalytic  $CO_2$  cycloaddition reactions based on 1. The  $CO_2$  cycloaddition with epoxides was performed under 1 atm pressure because 1 has a good affinity toward  $CO_2$ .

In a typical experiment, CO<sub>2</sub> cycloaddition with epichlorohydrin was chosen as a model reaction to optimize the reaction conditions. As shown in Table 1, the pure 1 or cocatalyst TBAB showed a low catalytic efficiency for the CO<sub>2</sub> cycloaddition with epichlorohydrin at room temperature (Table 1, entries 1 and 2). The catalytic performance of 1 together with cocatalyst TBAB exhibited a positive correlation with the increase of reaction temperature and reaction time. For example, the yields of cycloaddition in the presence of 1 (0.7)mol %) and TBAB (1.0% mol) increased from 80 to 93% with the reaction time extending from 48 to 72 h at 25 °C (Table 1, entries 3 and 4). The yield, however, was up to 77% at 50 °C and 99% at 90 °C only over 3 h (Table 1, entries 5 and 6), respectively. The catalytic performance exceeded the benchmark of other reported poly(ionic liquid) with similar yield under higher pressure of 1 MPa.<sup>11</sup> On the other hand, 1 is also

able to efficiently promote this  $CO_2$  cycloaddition in the absence of cocatalyst TBAB. As indicated in Table 1 (entries 7–10), the maximal yield is 80% at 50 °C over 48 h. When the reaction was carried out at 90 °C, the yield increased to 88% within 8 h (Table 1, entries 12 and 13). Notably, a 95% yield of the carbonate product was obtained at 90 °C in 12 h with 1.5 mol % amount of 1 (Table 1, entries 14–16).

The scope and generality of the present catalytic CO<sub>2</sub> cycloaddition can be further extended to other kinds of epoxides. Under the optimized reaction conditions, cycloaddition of CO<sub>2</sub> with epibromohydrin gave excellent yields with or without TBAB (Table 2, entries 1 and 2), which are comparable with those of epichlorohydrin. For substrate of styrene oxide, the corresponding cyclic carbonate was obtained in 51% yield in the presence of only 1 (1.5 mol %, Table 2, entry 5). However, the yield was significantly improved (up to 98%) by addition of the cocatalyst TBAB (Table 2, entry 6). Similarly, the reaction of glycidyl phenyl ether with CO<sub>2</sub> gave a moderate yield (52%, Table 2, entry 7) catalyzed by only 1 under the reaction conditions, while the cyclic carbonate was obtained in 99% yield with the assistance of TBAB (Table 2, entry 8). Compared to aromatic epoxides, the long chain substituted epoxide 1,2-epoxydecane, however, gave much lower yields even in the presence of TBAB as cocatalyst (entries 9 and 10), which might result from the weak interactions between the substrates and the MOF framework.

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For further confirming catalytic function of 1, a series of control experiments were carried out. The related results are summarized in Table 3. As shown in Table 3, almost no catalytic activity of pure UiO-67 has been observed even when the reaction was performed at 90 °C for 8 h (yield, <3%, Table 3, entries 1 and 2). The carbonate was obtained only in 8% yield even after 14 h (Table 3, entry 3). In contrast, 1 with imidazolium groups gave an excellent yield of 95% under the same conditions (Table 1). On the other hand, the UiO-67-TBAB catalytic system led to an incremental yield for epichlorohydrin CO2 cycloaddition as time went on, and arrived at a maximal yield of 98% over 14 h (Table 3, entries 4-6); meanwhile the 1-TBAB system afforded 99% yield within only 3 h (Table 1). Therefore, the embedded imidazolium group in 1 did play a key role in this CO<sub>2</sub> cyclic addition reaction.

In order to gain insight into the heterogeneous nature of 1, the hot leaching test was performed. As shown in Figure 5, no further reaction occurred without 1 after initiation of the epichlorohydrin  $CO_2$  cycloaddition at 2.5 h, indicating that no leaching of the catalytically active sites occurs and that 1 features a typical heterogeneous catalyst nature. After that, we examined the recyclability of 1. After each catalytic run, the solid catalyst of 1 could be easily collected by centrifugation, washed with ethanol, dried at 90 °C, and reused in the next run under the same conditions. Within five catalytic runs, yields of between 99 and 96% were obtained (Figure 5). The PXRD patterns of 1 and those after reuse within five catalytic runs indicate that the structural integrity of 1 was well-preserved (Figure 5).

Table 4 shows some recent progress of MOF and MOF– TBAB heterogeneous catalysts for  $CO_2$  cycloaddition of epichlorohydrin. Compared to various reported MOF catalysts (Table 4), 1 herein exhibits very good catalytic performance for this  $CO_2$  cyclic addition in the form of catalyst as either 1 or a 1–TBAB composite system. So, it could be a new valuable family member for MOFs to heterogeneous epoxide  $CO_2$ cycloaddition catalysts.

In summary, we report a new bifunctional robust and highly porous imidazolium-based ionic liquid decorated UiO-67 type MOF (UiO-67-IL, 1) which was prepared by a ligand-modification approach. It exhibits a highly selective adsorption for  $CO_2$  over  $CH_4$  and  $N_2$ . Furthermore, 1 herein can be used as a highly active heterogeneous catalyst for  $CO_2$  cycloaddition with epoxides under atmospheric pressure with or without cocatalyst TBAB (*n*-Bu<sub>4</sub>NBr).

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b03169.

Calculation of  $Q_{st}$  and <sup>1</sup>H NMR, FTIR, IR, and MS spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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